

	Type	L #	Hits	Search Text	DBs	Time Stamp	Comments
1	BRS	L1	10793	dehydrogenat\$5 with catalyst\$1	USPAT; EPO; JPO; DERWENT; IBMTDB	2002/04/01 15:59	
2	BRS	L2	5474	(feed\$1 or feedstock\$1) with (propane\$1 or ethane\$1 or butane\$1)	USPAT; EPO; JPO; DERWENT; IBMTDB	2002/04/01 16:00	
3	BRS	L3	3788	catalyst\$1 with (nio or ni?sub.2o?sub.3 or ni?sub.2o?sub.4 or (nickel\$1 adj1 oxide\$1))	USPAT; EPO; JPO; DERWENT; IBMTDB	2002/04/01 16:02	
4	BRS	L4	34	1 and 2 and 3	USPAT; EPO; JPO; DERWENT; IBMTDB	2002/04/01 16:02	

	Type	L #	Hits	Search Text	DBs	Time Stamp	Comments
1	BRS	L1	10793	dehydrogenat\$5 with catalyst\$1	USPA T; EPO; JPO; DERW ENT; IBM TDB	2002/04/01 15:59	
2	BRS	L2	5474	(feed\$1 or feedstock\$1) with (propane\$1 or ethane\$1 or butane\$1)	USPA T; EPO; JPO; DERW ENT; IBM TDB	2002/04/01 16:00	
3	BRS	L3	3788	catalyst\$1 with (nio or ni?sub.2o?sub.3 or ni?sub.2o?sub.4 or (nickel\$1 adj1 oxide\$1))	USPA T; EPO; JPO; DERW ENT; IBM TDB	2002/04/01 16:42	
4	BRS	L4	34	1 and 2 and 3	USPA T; EPO; JPO; DERW ENT; IBM TDB	2002/04/01 16:02	
5	BRS	L5	13118	(niobium near1 oxide\$1) or nb?sub.2o?sub.5 or (tantalum near1 oxide\$1) or ta?sub.2o?sub.5 or nb2o5 or ta2o5	USPA T; EPO; JPO; DERW ENT; IBM TDB	2002/04/01 16:40	
6	BRS	L6	0	4 and 5	USPA T; EPO; JPO; DERW ENT; IBM TDB	2002/04/01 16:40	

DOCUMENT-IDENTIFIER: US 6258992 B1

TITLE: Gas phase catalytic oxidation of hydrocarbons to carboxylic acids and dehydrogenated products

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ABPL:

Lower hydrocarbons are converted to carboxylic acids and/or dehydrogenated hydrocarbon product by contacting a feed mixture containing lower hydrocarbons, oxygen source, diluent, and sulfur-containing compound, with a multifunctional, mixed metal catalyst at a temperature from about 150.degree. C. up to about 400.degree. C. The lower hydrocarbons include C.sub.2 -C.sub.4, and the presence of sulfur compound in the feed mixture results in increased yield of carboxylic acid and/or dehydrogenated hydrocarbon product.

BSPR:

This invention relates to processes for low temperature catalytic oxidation of lower hydrocarbon feed to carboxylic acids and dehydrogenated product, particularly the conversion of ethane/ethylene to acetic acid or direct oxidation of ethane to vinyl acetate monomer over mixed metal oxide catalysts. The feed includes sulfur containing compound capable of producing oxides of sulfur. The process achieves a high yield of partial oxidation products.

BSPR:

Numerous processes are known for catalytic oxidation of ethane to oxygenated or oxy-dehydrogenated products. For example, U.S. Pat. No. 3,970,697, European Patent 627,401, European Patent Application 480,594 and International Application WO 99/13980 describe catalysts and processes for the production of

acetic acid from ethane and ethylene. U.S. Pat. Nos. 4,250,346, 4,524,236, 4,568,790, 4,596,787 and 4,899,003 describe catalysts and processes for oxydehydrogenation of ethane to ethylene. U.S. Pat. Nos. 4,370,492, 5,185,308, 4,902,823. and International Application WO 98/05620 describe catalysts and processes for the production of vinyl acetate from ethylene, acetic acid and oxygen. U.S. Pat. No. 4,339,355 describes catalysts and processes for the production of acrylic acid from acrolein. U.S. Pat. No. 4,148,757 describes catalysts for the ammoxidation of olefins to acrylonitrile and for the oxidation of olefins to acrolein and acrylic acid. In order to increase activity and product selectivity, most of the catalytic systems described in these disclosures include the addition of promoting metals to the catalysts rather than any process gas or co-feed as a promoter.

BSPR:

Oxidative dehydrogenation is a well known process for converting saturated or partially saturated organic compounds to corresponding compounds containing a greater degree of unsaturation. Yields of the reaction products are related to the type of the catalyst system and to the process conditions. Oxidative dehydrogenation processes utilizing sulfur oxide are described in U.S. Pat. Nos. 4,188,490 and 3,970,697. The catalysts used in the processes of U.S. Pat. Nos. 4,188,490 and 3,970,697 include palladium and gold on supports such as zinc oxide, alumina and silica; the catalyst is pre-treated with sulfur compound in moist air so that the concentration of sulfur-containing modifier is from about 0.05% to about 25% of the pre-treated, zinc oxide supported palladium and gold catalyst composition.

BSPR:

Accordingly, it would be desirable to provide a low temperature method which can have a significant impact on the productivity of the required products without effecting the integrity of the mixed metal oxide catalysts.

BSPR:

It is another object of the invention to produce vinyl acetate monomer (VAM) directly through ethane oxidation using sulfur containing compounds as a promoters in the presence of mixed metal oxide catalyst at particular process conditions.

BSPR:

The process of the present invention is a low temperature catalytic process for the production of oxygenated/oxydehydrogenated products by vapor phase oxidation of lower hydrocarbons using a small amount of sulfur-containing compounds such as hydrogen sulfide, sulfur dioxide or carbonyl sulfide in the feed. The process is carried out in the presence of multi-component, mixed metal redox catalysts. The invention using sulfur compounds in the feed can also be utilized in oxidation/ammoxidation of propane/propylene and direct production of vinyl acetate monomer from the conversion of ethane to ethylene followed by oxidation of ethylene with acetic acid.

BSPR:

The invention relates to a low temperature catalytic process, where a reactant feed comprising alkane (C_{2} , C_{3} , C_{4}), oxygen, sulfur-containing compound such as hydrogen sulfide, sulfur dioxide or carbonyl sulfide, and optionally water, is contacted in a vapor phase with a mixed metal oxide catalyst preferably having a composition selected from

BSPR:

The numerical values a, b, c and d represent the relative gram-atom ratios of the elements, Mo, V, Nb and X, respectively, in the catalyst. The elements are preferably present in combination with oxygen in the form of various oxides. This composition is described in U.S. Pat. No. 6,013,597 which is herein incorporated by reference.

BSPR:

The numerical values a, b, c and d represent the relative gram-atoms ratios of the elements, Mo, V, Nb and Pd, respectively, in the catalyst. The elements are preferably present in combination with oxygen in the form of various oxides. This composition is described in U.S. Pat. No. 5,907,056 which is herein incorporated by reference.

BSPR:

The numerical values a, b, c, d, e and f represent the relative gram-atom ratios of the elements, Mo, V, La, Pd, Nb and X, respectively, in the catalyst. The elements are preferably present in combination with oxygen in the form of various oxides. This composition is described in U.S. Pat. No. 6,060,421.

BSPR:

The numerical values of a, b, c, d, e and f represent the relative gram-atom ratios of the elements Mo, V, Ga, Pd, Nb and X respectively, in the catalyst. The elements are present in combination with oxygen in the form of various oxides. This composition is described in U.S. Pat. No. 6,114,278 which is herein incorporated by reference.

BSPR:

The numerical values of a, b, c, d, e and f represent the relative gram-atom ratios of the elements Mo, V, La, Pd, Nb and X respectively, in the catalyst. The elements are present in combination with oxygen in the

feed mixture
containing ethane:oxygen:nitrogen:H.sub.2 S:CO₂ in a
proportion of 40:8:52:0:0.
Reaction product showed the following results:

DEPR:

Calcined mixed metal oxide catalyst with a composition
Mo.sub.1 V.sub.0.398
La.sub.7.08e-6 Pd.sub.0.190e-04 Nb.sub.0.125 Al.sub.0.226
was prepared and
formulated into uniform particles of the 40-60 mesh size.
Catalyst was
evaluated at a temperature of 280.degree. C./200 psi with
feed mixture
containing ethane: oxygen: nitrogen:H.sub.2 S:CO₂ in a
proportion of
40:8:51:0.6:0.40. Reaction product showed the following
results:

DEPR:

Catalytic data demonstrate that a small concentration of
sulfur containing
compound yields a high productivity of partial oxidation
product in reactions
over mixed metal oxide catalysts at low temperature. This
low temperature
catalytic process is applicable for the oxidation or
ammoxidation of other
hydrocarbons such as propane and butane. Furthermore, this
high productivity
process can also be applied as a first stage process for the
production of equal
molar amounts of ethylene and acetic acid from ethane and
then feeding the
reactor outlet product to a vinyl acetate monomer (VAM)
reactor containing
conventional Pd/Au catalyst or mixed metal oxide catalysts
for the production
of VAM.

CLPR:

1. A gas phase process for the catalytic oxidation of
hydrocarbons to
carboxylic acids and dehydrogenated product said process
comprising contacting
a feed mixture comprising hydrocarbons selected from the
group consisting of
C.sub.2, C.sub.3 and C.sub.4 alkanes and alkenes and

form of various oxides. This composition is described in U.S. Pat. No. 6,143,928 which is herein incorporated by reference.

BSPR:

In one embodiment of the invention, a mixture comprising ethane, steam, sulfur-containing compound and oxygen or a compound capable of providing oxygen in the presence of mixed metal oxide catalysts, are reacted in a first reaction zone to provide a stoichiometric first product mixture comprising ethylene, oxygen, steam and acetic acid in high productivity. The first product mixture is fed into a second reaction zone in which the ethylene and acetic acid react in the presence of vinyl acetate monomer (VAM) catalyst to form vinyl acetate. The VAM catalyst can be chosen from VAM catalysts conventional in the art. The first product mixture can be fed directly into the second reaction zone without adding additional components, or the first product mixture can be adjusted by the addition of ethylene, acetic acid or oxygen. Moreover, the first product mixture can be subjected to temperature and/or pressure adjustment prior to being fed into the second reaction zone.

DEPR:

Catalytic oxidation processes using the mixed metal oxide catalyst and co-feed of sulfur promoter were carried out in a tubular reactor. All experiments were run at a temperature of 280.degree. C. and a pressure of about 200 psi.

DEPR:

Calcined mixed metal oxide catalyst with a composition Mo.sub.1 V.sub.0.398 La.sub.7.08e-6 Pd.sub.0.190e-04 Nb.sub.0.125 Al.sub.0.226 was prepared and formulated into uniform particles of the 40-60 mesh size. Catalyst was evaluated at a temperature of 280.degree. C./200 psi with

mixtures thereof, oxygen,
diluent and sulfur-containing compound with a mixed metal
oxide catalyst, said
contacting at a temperature of 150.degree. C. to
400.degree. C., under
conditions sufficient for gas phase oxidation.

CLPR:

3. The process of claim 1 where the mixed metal oxides
catalyst is selected
from the group consisting of

CLPR:

13. The process of claim 1, wherein said process comprises
reacting ethane
with steam, sulfur-containing compound and oxygen or a
compound capable of
providing oxygen, in the presence of mixed metal oxide
catalysts in a first
reaction zone to produced a stoichiometric first product
mixture comprising
ethylene, oxygen, steam and acetic acid, and said first
product mixture is fed
into a second reaction zone wherein the ethylene and acetic
acid react to form
vinyl acetate in the presence of vinyl acetate monomer
producing catalyst.

CLPR:

15. The process of claim 13, wherein said first product
mixture is fed into
said second reaction zone with addition or adjustment of
amounts of ethylene or
acetic acid or oxygen.

CLPL:

the numerical values of a, b, c, d, e and f represent the
relative gram-atom
ratios of the elements Mo, V, Ga, Pd, Nb and X respectively
in the catalyst and
these elements are present in combination with oxygen in
the form of oxides;
or

CCXR:

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